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Chromatographic Methods for Analysis of Ethylene Oxide in Emissions from Stationary Sources

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Abstract

Chromatographic methods of analysis with FID detection are investigated for quantitation of ethylene oxide in emissions from production plants and commercial sterilizers. A column with a stationary phase of 3% Carbowax 20M on 80–100 Chromosorb 101 is used to separate ethylene oxide from potential interferents in emissions from production plants. Two columns are found that allow accurate quantitation of ethylene oxide in emissions from commercial sterilizers. Both columns elute ethylene oxide before Freon 12, the diluent in the sterilization process. One column has a stationary phase of 1% SP-1000 on 60–80 Carbopack B and can be used to quantitate ethylene oxide over a wider range of concentrations than the other column, 5% Fluorcol (a fluorinated oil) on 60–80 Carbopack B. Graphitized carbon, the solid support in both of these columns, appears to participate in the ethylene oxide–Freon 12 separation with the SP-1000 column but not with the Fluorcol column.

Introduction

Ethylene oxide (EO) has been identified as a suspected human carcinogen (1). The Environmental Protection Agency declared its intent to list EO as a hazardous air pollutant under Section 112 of the Clean Air Act (2). This action requires the EPA to determine whether or not emission standards must be established to control EO emissions. To make this determination, the EPA conducted a study (3) in which commercial sterilizer operations and plants producing EO and its derivatives were considered as possible sources to be regulated. This study led us to the development of methods for sampling and analysis of EO from these sources so as to be able to support potential regulations. The literature showed that GC with photoionization detection has been used to monitor EO emissions during the operation of commercial sterilizers (4,5). However, the technique limits the column temperature to ambient temperature. This restriction could hamper the column's ability to resolve interferents. Infrared spectroscopy has been used to monitor EO, but only at low ppm levels (6). Integrated methods based on adsorbing EO on charcoal, followed by sample workup and analysis by GC–FID, are available (7,8). Integrated collection methods based on derivative formation and analysis by GC–ECD are also available (9,10). However, all of these integrated methods suffer from the disadvantages, relative to direct monitoring methods, of higher labor costs due to the sample preparation requirements and, more importantly, lack of real-time concentration data.

Therefore, direct sampling of emissions with analysis by GC–FID was chosen as the method to be evaluated. The evaluation emphasized the ability of GC columns to resolve the particular interferences encountered in sampling EO emissions. Work on the development of sampling methodology will be published elsewhere.

Experimental

Laboratory Experiments. A Hewlett-Packard Model 5830A GC and a Varian Model 3400 GC, both equipped with FIDs and sample loops, were used in the laboratory evaluation. The latter GC was equipped with a heated sample valve. EO in air and EO and Freon 12 mixtures in air were prepared in Tedlar bags (2-mil thickness) by flow dilution of EO and Freon 12 (99+% in lecture bottles) with dry house air. The bags were equipped with on/off valves and a tubing connector to allow withdrawal of samples with a syringe for injection into the GC. Aluminum cylinders containing EO and EO–Freon 12 mixtures (Scott Specialty Gases and MG Industries), the contents of which were certified by the supplier to be accurate to within 2%, were also used as a source of calibration and other samples.

EO–acetaldehyde mixtures were generated by sampling the atmosphere above a reagent bottle of acetaldehyde with a glass syringe and then injecting the sample into an unheated sample loop so that acetaldehyde (bp 21 °C) would condense. Then EO-in-air atmospheres were injected into the loop, and the resultant EO–acetaldehyde atmosphere was chromatographed until the desired ratio of EO to acetaldehyde was obtained. Other potential EO interferents were tested by injecting the interferent into Tedlar bags containing an EO–air atmosphere and chromatographing the resultant atmosphere.

Field Experiments. A Varian Model 3400 GC equipped with dual FIDs and with a Nutech heated valve box containing two six-port sample valves was used in both field tests. A 0.25-cm³

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sample loop was used for sampling the sterilizer charge, and a 2.0-cm³ sample loop was used to sample the sterilizer emissions. The FID electrometers were connected to Shimadzu C-RIA integrators. Typical calibration curves for quantitating EO emissions and EO in the sterilizer charge are shown in Figures 1 and 2, respectively.

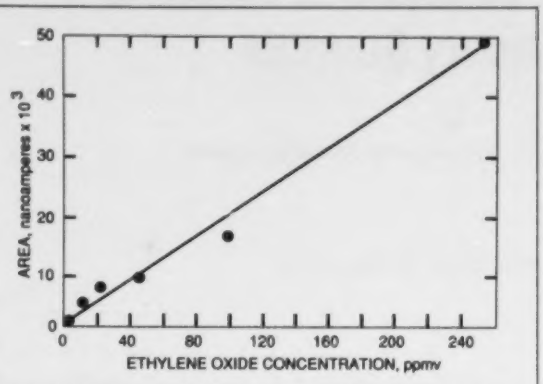

Figure 1. Ethylene oxide calibration curve. The curve is for quantitating ethylene oxide emissions when using the 1% SP-1000 column.

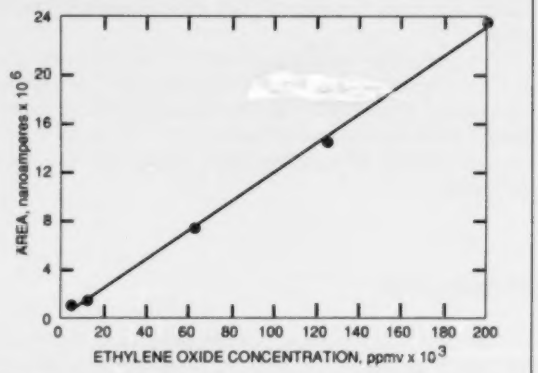

Figure 2. Ethylene oxide calibration curve. The curve is for quantitating ethylene oxide in the sterilizer charge when using the 1% SP-1000 column.

Results and Discussion

Production and derivative plants.

The first sources investigated were production and derivative plants. EO is produced by oxidation of ethylene with a silver catalyst (3). A small amount of acetaldehyde, 0.005–0.025 wt% of the EO, is also produced. Other potential interferents from these two processes are listed in Table I. Since it did not appear that these compounds would elute near EO and since acetaldehyde and EO are isomers, initial work was directed toward

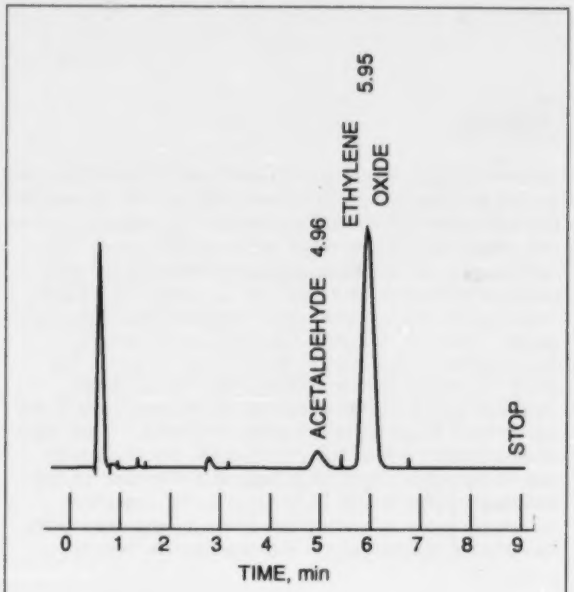

Figure 3. Separation of acetaldehyde from ethylene oxide. GC conditions as described in Table I.

Table I. The Evaluation of Potential Interferents in the Analysis of EO*

Potential interferent	Retention time (min)			Comments
	Interferent	EO	R†	
Acetaldehyde‡	3.3	3.9	1.4	Acetaldehyde response 24% of EO response
Acetaldehyde	4.9	5.9	2.5	Acetaldehyde response 20% of EO response
Acetaldehyde§	5.4	6.5	2.5	Acetaldehyde response 37% of EO response
Methyl chloride	3.4	5.9	7.5	Base line resolution
Ethanol	8.6	5.9	5.0	Ethanol response 47% of EO response
Ethanol§	9.5	6.6	4.8	Ethanol response 350% of EO response
Ethane	1.2	6.0	12	
Ethylene	1	6.0	12	
2-Aminoethanol§	16	—	—	Very broad peak
2-Methoxyethanol	62	5.9	—	
2-Butoxyethanol	73	—	—	Very broad peak
1-Butanol	76	6.1	—	

* The column was 3% Carbowax 20M on 80–100 Chromosorb 101, 10 ft × ⅛ in. s.s. Other GC conditions were as follows: carrier gas, N_2 at 36 cm³/min; sample loop volume, 3.0 cm³; oven temperature, 85°C isothermal; injector temperature, 85°C; detector, FID at 200°C. The ethylene oxide concentration was 4 to 8 ppm (v/v) in air. The retention times are unadjusted; the methane retention time was 0.9 min.

† $R = 2d/(w_1 + w_2)$.

‡ Six-foot column.

§ at 30 cm³/min.

separating the two isomers. A packed column containing 3% Carbowax 20M on 80–100 Chromosorb 101 produced base line resolution (R = 2.5) of the two isomers at 85 °C, as shown in Figure 3. No attempt was made to control the acetaldehyde concentration. Rather, an excess of the anticipated amount was generated by using the procedure described in the Experimental section, and the acetaldehyde concentration was approximated by calculating the response as a percent of the EO response. The base line resolution of the two isomers was obtained at acetaldehyde "concentrations" of 20 and 37% of the EO concentration. Even considering possible differences in FID response for the two compounds, the acetaldehyde concentration still represents a large excess over the anticipated amount. The results of testing the other potential interferents with the 3% Carbowax 20M column are also shown in Table I. None of these compounds interfered with EO resolution. The compound that came the closest to being an interferent was ethanol (R = 4.8). The limit of detection for this procedure was 0.04 ppm as determined both by the method of Knoll (11) and by doubling the noise level.

The next phase of this work involved preparing synthetic EO–air mixtures in Tedlar sampling bags and testing the stability of the EO concentration. The bags were stored both under laboratory conditions and exposed to the ambient atmosphere. The bags exposed to the atmosphere were stored in a smog chamber to protect the bags from wind damage. After two days of storage, a new peak appeared in the samples that were stored exposed to the atmosphere. This new peak was absent in the samples stored under laboratory conditions. The peak was identified, by retention time and peak shape, as acetaldehyde. Acetaldehyde has been identified as a minor product of the photolysis of EO (12,13). After 21 days of storage, all of the bags that had been exposed to the atmosphere (sunny conditions existed less than half of the time) were lower in EO concentration than comparable bags that were not exposed to sunlight. The decrease in EO concentration was only 4–9%. However, under conditions of sustained exposure to sunlight, the decrease in EO concentration should be greater. Thus, to achieve optimum EO stability, exposure of the sample to sunlight should be minimized.

The next step in the method development process would have been field testing, but it was concluded that the nationwide EO emissions from production and derivative plants were not large enough to justify regulation. However, the results of the above work may be of interest to personnel in industry involved in sampling and analysis of EO at production and derivative plants to monitor process conditions or to determine compliance with state-imposed regulations.

Commercial Sterilizers

The next source to be considered was commercial sterilizers (3), and further work on method development was directed at this source. The most common sterilant used in commercial sterilization operations is a mixture of 12% w/w (27% v/v) EO and 88% w/w (73% v/v) Freon 12 (dichlorodifluoromethane) (3). Sterilization is accomplished in a closed system. A typical chamber volume is 1000 ft^3 (3). Medical devices that can not withstand high-temperature sterilization are the most common items sterilized. The chamber is initially evacuated to approximately 2 psia, steam is added, and then the chamber is filled with the EO–Freon 12 mixture. After sterilization is complete, the chamber is evacuated with a vacuum pump, and the emissions are passed through a control system containing dilute H_2SO_4. The EO is converted to ethylene glycol with greater than 99% efficiency. The Freon 12 passes through the control system unchanged. Thus, in the first evacuation cycle, where no air has been added, the emissions will contain a high concentration of Freon 12 and a low concentration of EO. The first experiment with this system involved chromatographing a sample of these emissions on one of the columns that had been reported to resolve the EO and Freon 12 peaks (14). GC–FID was used. The column was Porapak R 100–120 mesh, 6 ft × $^1/_4$ in. s.s., operated at 100 °C isothermal. A high concentration of Freon 12 eluted first, and the EO appeared as a shoulder on the tail of the Freon 12 peak. Therefore, a column that would reverse the order of elution was needed to accurately quantitate the EO over the range of concentrations expected in the emissions.

The next series of experiments involved evaluating different stationary phases, using GC–FID, for their ability to elute EO before Freon 12. Finely divided carbon particles packed into a Teflon column have been shown to elute EO before Freon 12 (4). Synthetic atmospheres consisting of mixtures of EO and Freon 12, prepared in Tedlar bags, were used as samples for evaluating the different columns. Two stationary phases, a graphitized carbon (Carbopack BHT) and a fluorinated oil (Fluorcol), were found to elute EO before Freon 12. Both columns were 10 ft × $^1/_4$ in. s.s. The Fluorcol column contained 5% Fluorcol on 60–80 Carbopack B. The Fluorcol column showed a higher number of theoretical plates for resolving EO than did the Carbopack BHT column (2560 compared to 1940) and was less sensitive to overloading. Therefore, further work was continued with the Fluorcol column. This column was developed for the separation of mixtures of Freons (15). HETP values showed that the column was less efficient at resolving EO than Freon 12, as expected. The elution of the Freon 12 after the EO is apparently caused by strong dipole–dipole interaction between the Fluorcol and the Freon 12. This is apparent when one considers the fact that the boiling point of Freon 12 is 39° lower than that of EO.

The next step in the methods development process involved field testing at a commercial sterilizer. The test involved on-line GC–FID determination of EO and Freon 12 concentrations in the emissions downstream from the control system. The EO and Freon 12 concentrations were also determined upstream from the control system, i.e., in the sterilizer charge. These two measurements, and the necessary volumetric data, allowed us to determine the control system efficiency for EO. (Quantitating the Freon 12 was necessary to determine the gas molecular weight, which in turn was needed to obtain accurate measurements of the gas flow rate out of the control system.) Chromatograms of samples taken from the sterilizer emissions and the sterilizer charge are shown in Figures 4 and 5, respectively. Under both conditions, at an oven temperature of 100 °C, the EO eluted first, and baseline resolution from the Freon 12 was obtained. During quantitation of the emissions, it was observed that the EO retention time increased gradually (by 0.3 min) as the EO concentration decreased. The shifting EO retention time made identification of this peak difficult and necessitated the injection of multiple concentration standards to allow identification of the EO peak. Earlier laboratory studies suggested that, at the optimum column temperature of 65 °C, the EO retention time was less sensitive to change as a function of EO concentration. A column temperature of 100 °C was necessary in the field experiments to reduce analytical time and thereby max-

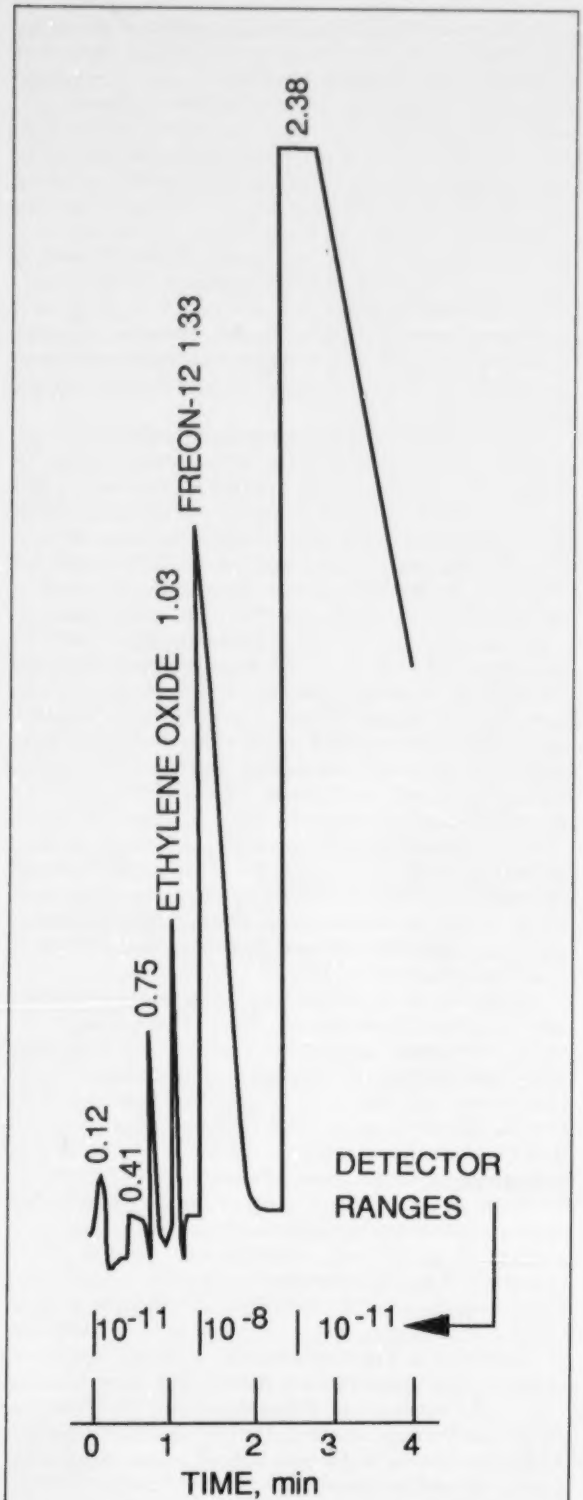

Figure 4. Chromatogram of sample from sterilizer emissions. Sample taken 9 min into first evacuation. GC conditions: sample loop, 2.0 cm^3 at 180°C; flow rate, 30 cm^3 N_2/min; oven temperature, 100°C. EO concentration, 32 ppmv. Freon 12 concentration, 70% (by volume).

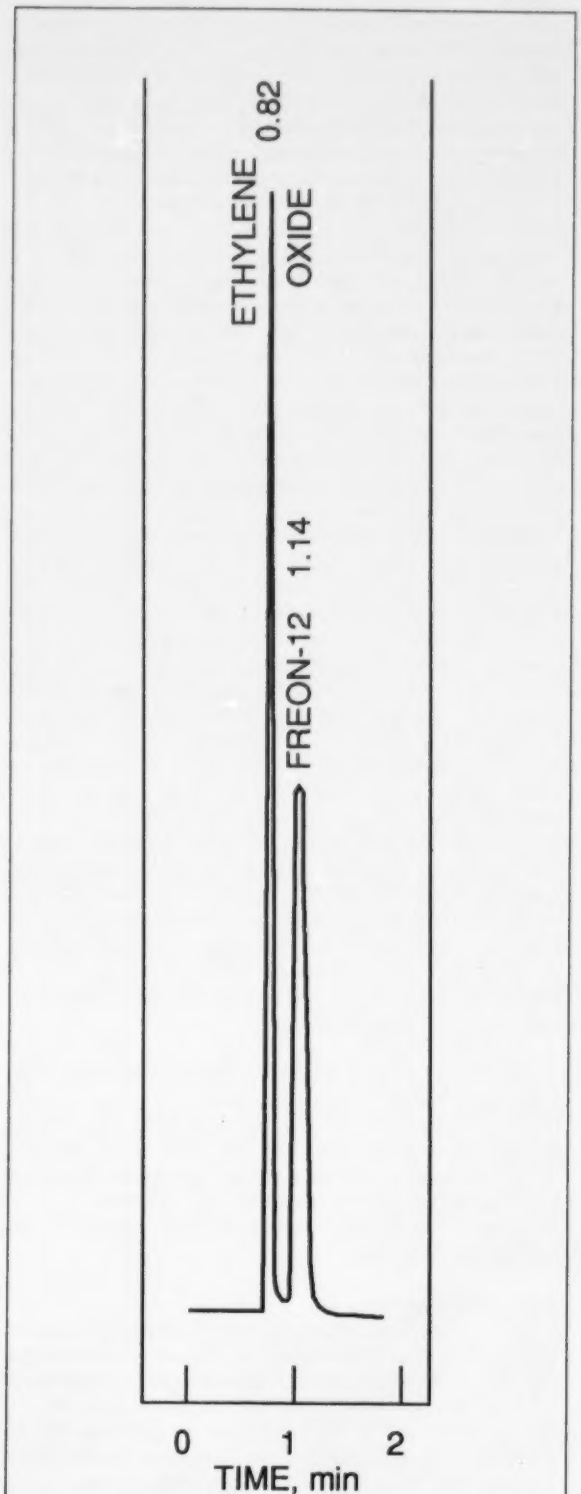

Figure 5. Chromatogram of sample from sterilizer charge. Sample taken 9 min into first evacuation. GC conditions: sample loop, 0.25 cm^3 at 180°C; flow rate, 60 cm^3 N_2/min; oven temperature, 100°C. EO concentration, 32% (by volume). Freon 12 concentration, 72% (by volume).

imize the number of samples obtained during each chamber evacuation. Apparently, the higher column temperature and the high Freon 12 concentration in the sample reduced the efficiency of the column with respect to EO.

Since the separation between EO and Freon 12 was 0.3 min (Figure 4), the observed shift in retention time as a function of EO concentration needed to be reduced to provide accurate identification of the EO peak in a complex chromatogram, such as that shown in Figure 4.

The next step in the methods development process involved off-line sampling, as opposed to the on-line sampling procedure used earlier. With the off-line sampling procedure, grab samples were taken in Tedlar bags and accumulated for analysis. In this way, an adequate number of samples could be obtained, and the column could be used under conditions of optimum efficiency. The experiments involved sampling emissions from the same commercial sterilizer that was sampled in the earlier work. Two different columns were evaluated: the Fluorcol column and a 6 ft × $^1/_8$ in. s.s. column containing 1% SP-1000 on 60–80 Carbopack B. The latter column had previously been reported

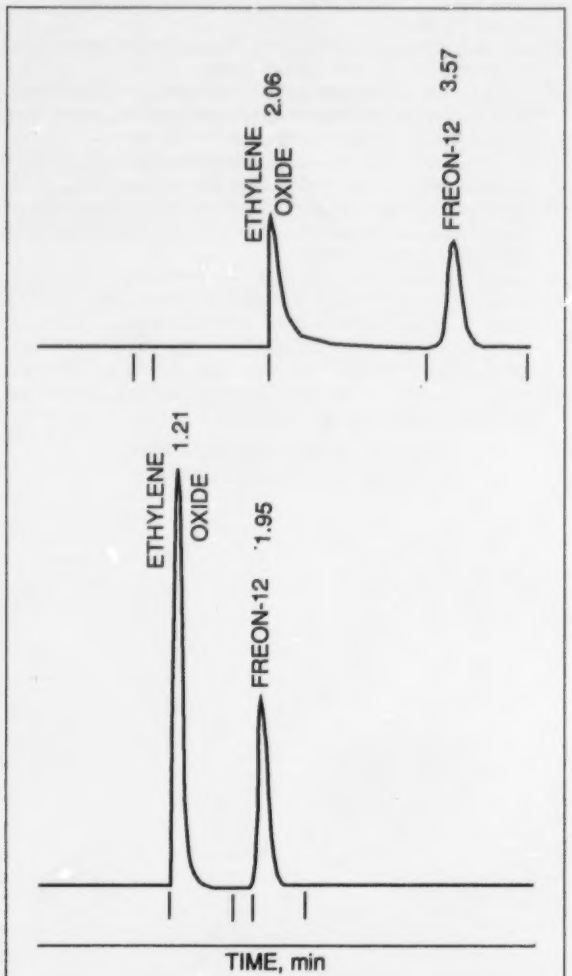

Figure 6. Chromatograms of 2510-ppmv EO and 6020-ppmv Freon 12 on 5% Fluorcol on 60–80 Carbopack B, 10 ft × $^1/_8$ in. s.s. (top) and 1% SP-1000 on 60–80 Carbopack B, 6 ft × $^1/_8$ in. s.s. (bottom). GC conditions: oven temperature, 65°C; flow rate, 30 cm³ N_2/min.

to elute EO before Freon 12 (16). At a column temperature of 65°C, the shift in retention time with changing EO concentration was reduced slightly (to 0.2 min) with the Fluorcol column. However, the SP-1000 column showed only a negligible (0.1-min) shift in the EO retention time over a concentration range of 65 to 1400 ppm EO. A subsequent laboratory study over a wider range of EO and Freon 12 concentrations confirmed that the SP-1000 column produced stable EO retention times, and that the Fluorcol column produced a large variation in EO retention times. The efficiency of the two columns was determined by calculating HETP values. The results showed that the SP-1000 column was more efficient than the Fluorcol column at ppm levels of EO. It should be noted that, at high per cent levels (12.5%) of EO, the Fluorcol column had the lowest HETP values. Thus, the HETP values complement the retention time data. The improved efficiency obtained with the SP-1000 column can be seen in the chromatograms in Figure 6 where both EO and Freon 12 produced narrower peaks with no tailing when compared, under the same conditions, with the Fluorcol column. The optimum conditions for using both columns are given in Table II.

In view of the apparent mechanism by which the EO and Freon 12 are separated on the Fluorcol column, it was surprising that a polar stationary phase such as SP-1000 would apparently elute these two compounds in the same order. However, both the SP-1000 and Fluorcol columns contain graphitized carbon (Carbopack) as the solid support, and graphitized carbon itself will elute EO before Freon 12. This observation, plus the fact that the SP-1000 concentration was only 1%, suggests that the graphitized carbon is participating in the separation. At this low loading, the SP-1000 would appear to be preferentially adsorbed on areas of the carbon surface having the highest heat of adsorption, i.e., chemical impurities. Therefore, the remaining surface area would be present as carbon which is where the EO–Freon 12 separation occurs. The participation of graphitized carbon in separations when used as a solid support in gas–liquid chromatography has been discussed in the literature (17). With the Fluorcol column at a concentration of 5%, the graphitized carbon surface would appear to be completely covered, the separation taking place by interaction with the Fluorcol.

The limit of detection (11) for the 1% SP-1000 and 5% Fluorcol columns was the same, 0.15 ppm EO. The lowest EO concentration determined was 1.0 ppm.

Conclusions

A column was found that will separate interferences from ethylene oxide in emissions from ethylene oxide production

Table II. Optimum Conditions for Using the 1% SP-1000 and 5% Fluorcol Columns*

Stationary phase	1% SP-1000 on 60–80 Carbopack B	5% Fluorcol on 60–80 Carbopack B
Column dimensions	6 ft × $^1/_8$ in. s.s.	10 ft. × $^1/_8$ in. s.s.
Column temperature	45°	65°
EO concentration for optimum column efficiency	0 to 2500 ppmv	>12.5 vol %
Linearity	0.5 to >20 vol %	0.1 to >50 vol %
Detector	FID	FID

* Carrier gas is N_2 at 30 cm³/min for both columns.

plants and allow accurate quantitation of the compound. Also, two columns were found that will allow accurate quantitation of EO in emissions from commercial sterilizers. One column based on SP-1000 can be used to quantitate EO over a wider range of concentrations than the other column, which is based on a fluorinated oil. Graphitized carbon, the solid support in both of these columns, appears to participate in the separation with the SP-1000 column but not in the separation with the Fluorcol column.

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